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James R. Durig
University of Missouri - Kansas City, sapeebles@eiu.edu

Savitha S. Panikar
University of Missouri - Kansas City

Daniel A. Obenchain
Eastern Illinois University

Brandon J. Bills
Eastern Illinois University

Patrick M. Lohan
Eastern Illinois University

See next page for additional authors

Authors
James R. Durig, Savitha S. Panikar, Daniel A. Obenchain, Brandon J. Bills, Patrick M. Lohan, Rebecca A. Peebles, Sean A. Peebles, Peter Groner, Gamil A. Guirgis, and Michael D. Johnston

Microwave, infrared and Raman spectra, r_0 structural parameters, *ab initio* calculations and vibrational assignment of 1-fluoro-1-silacyclopentane[a)]

James R. Durig,[1,b)] Savitha S. Panikar,[1] Daniel A. Obenchain,[2] Brandon J. Bills,[2] Patrick M. Lohan,[2] Rebecca A. Peebles,[2] Sean A. Peebles,[2] Peter Groner,[1] Gamil A. Guirgis,[3] and Michael D. Johnston[3]

[1]*Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110, USA*
[2]*Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920, USA*
[3]*Department of Chemistry and Biochemistry, College of Charleston, Charleston, South Carolina 29424, USA*

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The microwave spectrum (6500–18 500 MHz) of 1-fluoro-1-silacyclopentane, c-C_4H_8SiHF has been recorded and 87 transitions for the ^{28}Si, ^{29}Si, ^{30}Si, and ^{13}C isotopomers have been assigned for a single conformer. Infrared spectra (3050-350 cm^{-1}) of the gas and solid and Raman spectrum (3100-40 cm^{-1}) of the liquid have also been recorded. The vibrational data indicate the presence of a single conformer with no symmetry which is consistent with the *twist* form. *Ab initio* calculations with a variety of basis sets up to MP2(full)/aug-cc-pVTZ predict the *envelope-axial* and *envelope-equatorial* conformers to be saddle points with nearly the same energies but much lower energy than the *planar* conformer. By utilizing the microwave rotational constants for seven isotopomers (^{28}Si, ^{29}Si, ^{30}Si, and four ^{13}C) combined with the structural parameters predicted from the MP2(full)/6–311+G(d,p) calculations, adjusted r_0 structural parameters have been obtained for the *twist* conformer. The heavy atom distances in Å are: $r_0(SiC_2) = 1.875(3)$; $r_0(SiC_3) = 1.872(3)$; $r_0(C_2C_4) = 1.549(3)$; $r_0(C_3C_5) = 1.547(3)$; $r_0(C_4C_5) = 1.542(3)$; $r_0(SiF) = 1.598(3)$ and the angles in degrees are: $\angle CSiC = 96.7(5)$; $\angle SiC_2C_4 = 103.6(5)$; $\angle SiC_3C_5 = 102.9(5)$; $\angle C_2C_4C_5 = 108.4(5)$; $\angle C_3C_5C_4 = 108.1(5)$; $\angle F_6Si_1C_2 = 110.7(5)$; $\angle F_6Si_1C_3 = 111.6(5)$. The heavy atom ring parameters are compared to the corresponding r_s parameters. Normal coordinate calculations with scaled force constants from MP2(full)/6–31G(d) calculations were carried out to predict the fundamental vibrational frequencies, infrared intensities, Raman activities, depolarization values, and infrared band contours. These experimental and theoretical results are compared to the corresponding quantities of some other five-membered rings. © *2012 American Institute of Physics*. [doi:10.1063/1.3673889]

I. INTRODUCTION

Many monosubstituted cyclopentanes have been determined to exist in two conformations in the fluid states at ambient temperature where the substituent occupies the *envelope-axial* and *envelope-equatorial* positions both with C_s symmetry. For several of these molecules, the vibrational spectra were used first to identify the two forms before they were identified by microwave spectra and/or electron diffraction studies. The monohalocyclopentanes are interesting examples where initially the fluoride, chloride, and bromide[1] were all reported to have these forms from analyses of their infrared spectra. Later, from an investigation of the Raman spectrum[2] of liquid fluorocyclopentane, it was concluded that there was only one conformer present in the fluid states and it was the *envelope-equatorial* conformer which was supported by the theoretical predictions[3] from the CNDO model. More recently, we[4] have shown from the infrared spectra of the gas and variable temperature xenon solutions that there is, indeed, only one conformer in the fluid phases but it is the *twist* (C_1 symmetry) form which was supported by structural parameters obtained from the rotational constants obtained from the microwave spectrum. However, both chlorocyclopentane[5] and bromocyclopentane[6] have been shown to have the *envelope-axial* and *envelope-equatorial* conformers as the two stable forms of these five-membered ring compounds.

We have determined the conformational stabilities from vibrational spectra of c-C_4H_8SiHCl (Ref. 7) and c-C_4H_8SiHBr (Ref. 8) and there is only one conformer, which is the *twist* form, for both of these molecules. However, the structural parameters have not been determined and there is very limited structural data available for the c-C_4H_8SiHX molecules. Therefore, we have continued our studies of the conformational stability of these molecules and we have chosen 1-fluoro-1-silacyclopentane for our next investigation where we will determine the conformational form or forms along with the determination of the r_0 structural parameters.

From this study we are reporting the microwave spectra for the ^{28}Si, ^{29}Si, ^{30}Si, and four ^{13}C isotopomers of c-C_4H_8SiHF. Also, we are reporting the infrared spectra of the gas and solid as well as the Raman spectrum of the liquid from which the relative conformational stabilities have been determined and vibrational assignments made. To aid the vibrational assignment and support the conformational stability

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[b)]Author to whom correspondence should be addressed. Electronic mail: durigj@umkc.edu. Telephone: 01-816-235-6038. Fax: 01 816-235-2290.

determination, we have carried out *ab initio* calculations at the MP2 level with full electron correlation by the perturbation method with a relatively large number of basis sets. Similarly, density functional theory calculations have also been carried out by the B3LYP method. The results of these spectroscopic and theoretical studies are reported herein.

II. EXPERIMENTAL AND THEORETICAL METHODS

The 1-chloro-1-silacyclopentane sample was prepared by adding a double Grignard reagent of 1,4-dibromobutane dissolved in 60 mL of anhydrous ethyl ether to a solution of trichlorosilane in anhydrous ethyl ether under nitrogen gas similar to the method of West.[9] The sample 1-chloro-1-silacyclopentane was then fluorinated with freshly sublimed antimony trifluoride without solvent to give the final product, 1-fluoro-1-silacyclopentane. The purity of the sample was checked by infrared and NMR data.

The rotational spectrum belonging to a single conformer of c-C_4H_8SiHF was measured in the 6500–18 500 MHz range on a 480 MHz bandwidth chirped-pulse Fourier-transform microwave spectrometer (CP-FTMW) at Eastern Illinois University. This instrument has been described in detail previously[10] and is a reduced bandwidth version of the original CP-FTMW spectrometer at the University of Virginia.[11] The rotational spectrum was scanned in 480 MHz segments, each an average of 5000 free induction decays. These segments were pasted together using a simple peak-picking routine written in LabVIEW (Ref. 12) to determine the absolute frequency of observed transitions. Spectra of a total of seven isotopologues were observed in natural abundance (corresponding to the three naturally occurring silicon isotopes (^{28}Si = 92.23%, ^{29}Si = 4.68%, ^{30}Si = 3.09%) and the four unique carbon substitutions (^{13}C = 1.11%) in the most abundant ^{28}Si species).

A sample consisting of roughly 0.4% c-C_4H_8SiHF diluted in He/Ne (82.5% Ne : 17.5% He, BOC gases) was prepared in a 2 L stainless steel tank and expanded through the 0.8 mm orifice of a general valve series 9 nozzle at a pressure of ~2 atm. The gas expansion entered the vacuum chamber perpendicular to the microwave horns of the CP-FTMW spectrometer and the observed rotational transitions had full-width at half maximum values of 130–150 kHz. Although these linewidths are up to 25 times larger than transitions measured on a typical resonant cavity instrument, the precision of frequency measurement is not significantly worse than our resonant cavity spectrometer (which also uses a perpendicular gas expansion), with transition frequencies on the CP-FTMW instrument being reproducible to within about 6 kHz (as is evident from the quality of the fits in Table I). The signal-to-noise ratios of the strongest transitions belonging to the ^{28}Si species were approximately 250 in 5000 averages.

An MP2(frozen core)/6–311++G(2d,2p) calculation using GAUSSIAN 03 program[13] was carried out to predict rotational constants for the observed conformer to aid in initial spectral assignment. Pickett's SPCAT/SPFIT spectral assignment programs,[14] along with Kisiel's AABS software package,[15,16] were used to predict and assign the spectra of all seven isotopologues, using a Watson *A* reduction Hamiltonian.[17] The spectroscopic parameters for these isotopologues of c-C_4H_8SiHF are listed in Table II. The smaller data sets for the ^{29}Si, ^{30}Si, and ^{13}C isotopic species required fixing of the centrifugal distortion constants at the values obtained from the B3LYP/6–311+G(d,p) calculations.

The mid-infrared spectra of the gas and solid (Fig. 1) were obtained from 3050 to 350 cm^{-1} on a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The theoretical resolution used to obtain the spectrum of the gas was 0.5 cm^{-1} and 128 interferograms were added and transformed with a boxcar truncation function. For the spectrum of the solid, a theoretical resolution of 2 cm^{-1} was used with 128 interferograms added and truncated. The assigned fundamentals from the infrared spectra are listed in Table III along with their predicted intensities and band contours.

The Raman spectra (Fig. 2) were recorded from 3100 to 40 cm^{-1} on a Spex model 1403 spectrophotometer equipped with a Spectra-Physics model 2017 argon ion laser operating on the 514.5 nm line. The laser power used was 1.5 W with a spectral bandpass of 3 cm^{-1}. The spectrum of the liquid was recorded with the sample sealed in a Pyrex glass capillary. Depolarization measurements were obtained for the liquid sample using a standard Ednalite 35 mm camera polarizer with 38 mm of free aperture affixed to the Spex instrument. Depolarization ratio measurements were checked by measuring the state of polarization of the Raman bands of CCl_4 immediately before depolarization measurements were made on the liquid sample. The measurements of the Raman frequencies are expected to be accurate to ±2 cm^{-1}. All of the observed bands

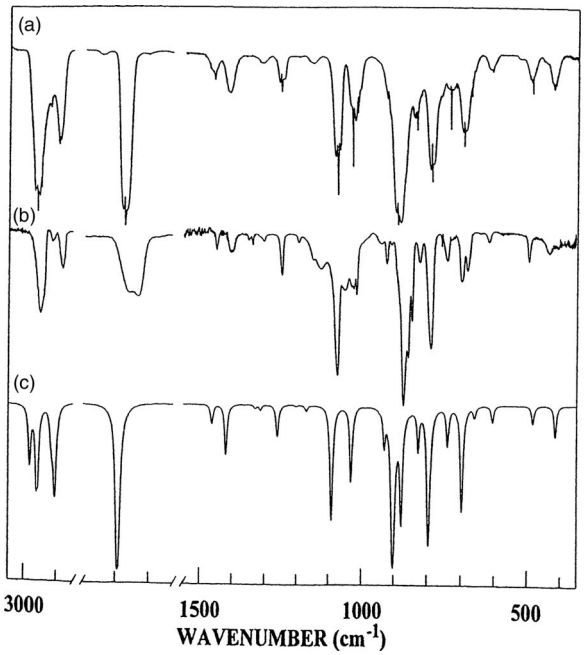

FIG. 1. Comparison of experimental and calculated infrared spectra of 1-fluoro-1-silacyclopentane: (a) observed spectrum of gas; (b) observed spectrum of solid; (c) simulated spectrum of *twist* (C_1) conformer.

TABLE I. Rotational transition frequencies (MHz) of the ground vibrational state of 1-fluoro-1-silacyclopentane.

	c-$C_4H_8{}^{28}$SiHF		c-$C_4H_8{}^{29}$SiHF		c-$C_4H_8{}^{30}$SiHF		$^{13}C_1$		$^{13}C_2$		$^{13}C_3$		$^{13}C_4$	
Transition	ν_{obs}	$\Delta\nu$[a]	ν_{obs}	$\Delta\nu$[a]	ν_{obs}	$\Delta\nu$[a]	ν_{obs}	$\Delta\nu$[a]	ν_{obs}	$\Delta\nu$[a]	ν_{obs}	$\Delta\nu$[a]	ν_{obs}	$\Delta\nu$[a]
$2_{21} \leftarrow 2_{11}$	6995.175	0												
$1_{10} \leftarrow 0_{00}$	7068.660	−1												
$2_{12} \leftarrow 1_{11}$	8079.092	−1	8057.223	−5	8035.901	−3	7984.115	1			8031.234	−4	8033.091	5
$2_{20} \leftarrow 2_{12}$	8452.754	−4												
$2_{02} \leftarrow 1_{01}$	8481.160	−1	8455.803	−3	8431.098	−5	8380.066	−3	8361.287	−6				
$2_{11} \leftarrow 1_{10}$	9008.924	1	8977.709	−1			8897.934	−1	8876.666	−2			8986.300	2
$3_{03} \leftarrow 2_{11}$	9247.458	2												
$2_{21} \leftarrow 2_{02}$	10 319.592	1												
$3_{22} \leftarrow 3_{03}$	10 563.743	5												
$4_{22} \leftarrow 4_{14}$	10 992.343	3												
$4_{23} \leftarrow 4_{04}$	11 084.291	−4												
$2_{11} \leftarrow 1_{01}$	11 805.579	2	11 769.236	−1	11 733.977	1								
$5_{24} \leftarrow 5_{05}$	11 958.104	1												
$3_{13} \leftarrow 2_{12}$	12 081.665	4	12 049.538	−4			11 940.281	2	11 913.567	3	12 006.766	8	12 009.729	3
$4_{32} \leftarrow 4_{22}$	12 141.959	1												
$4_{04} \leftarrow 3_{12}$	12 294.711	1												
$3_{03} \leftarrow 2_{02}$	12 571.871	0	12 536.534	−6	12 502.075	−5	12 424.559	−7	12 398.494	3	12 499.137	2	12 501.105	2
$3_{22} \leftarrow 2_{21}$	12 816.020	2	12 776.206	−4	12 737.441	−4								
$3_{30} \leftarrow 3_{22}$	12 863.055	1												
$4_{31} \leftarrow 4_{23}$	13055.227	−2												
$3_{21} \leftarrow 2_{20}$	13 060.093	−5	13 015.812	0	12 972.754	−12								
$3_{12} \leftarrow 2_{11}$	13 471.039	1	13 425.045	1	13 380.302	−5	13 305.873	0	13 274.645	2	13 434.569	−1	13 433.395	−3
$5_{05} \leftarrow 4_{13}$	14 766.559	1												
$5_{14} \leftarrow 4_{22}$	15 808.273	0												
$4_{14} \leftarrow 3_{13}$	16 046.888	3	16 005.137	2	15 964.392	3			15 825.295	−1	15 942.216	−4	15 946.481	−5
$2_{20} \leftarrow 1_{10}$	16 066.932	−2												
$2_{21} \leftarrow 1_{11}$	16 469.014	0												
$4_{04} \leftarrow 3_{03}$	16 518.289	−4	16 475.075	3	16 432.877	5	16 328.197	3	16 296.172	−1	16 405.057	0	16 408.782	0
$4_{23} \leftarrow 3_{22}$			16 986.708	8	16 935.917	4								
$3_{12} \leftarrow 2_{02}$	16 795.456	1												
$4_{32} \leftarrow 3_{31}$	17 199.216	−2												
$4_{31} \leftarrow 3_{30}$	17 231.026	1												
$4_{22} \leftarrow 3_{21}$	17 608.034	3	17 546.033	−5	17 485.799	10								
$4_{13} \leftarrow 3_{12}$	17 874.726	−5	17 815.164	6	17 757.187	2	17 657.294	2						

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$ in kHz.

TABLE II. Experimental rotational (MHz) and centrifugal distortion (kHz) constants of 1-fluoro-1-silacyclopentane isotopomers.

	^{28}Si	^{29}Si	^{30}Si	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$
A	4700.2018(6)	4690.778(5)	4681.667(7)	4616.87(4)	4614.95(3)	4681.98(3)	4664.14(3)
B	2368.4634(7)	2359.4914(5)	2350.7746(8)	2366.313(1)	2365.730(1)	2333.0102(8)	2338.7151(6)
C	1903.5467(5)	1899.2490(5)	1895.0468(7)	1888.3116(9)	1889.1224(7)	1877.6507(7)	1881.8034(8)
N[a]	33	14	12	6	7	8	8
ν_{rms}[b]	2.8	4.4	4.0	9.6	9.4	5.9	2.9

	MP2(full)/ 6–311+G(d,p)	B3LYP/ 6–311+G(d,p)	Expt.	B3LYP/6–311+G(d,p)					
Δ_J	0.666	0.642	0.727(11)	0.632	0.622	0.630	0.632	0.617	0.641
Δ_{JK}	−2.707	−2.711	−2.770(37)	−2.687	−2.661	−2.602	−2.608	−2.607	−2.746
Δ_K	5.973	6.060	6.121(57)	6.059	6.056	5.762	5.758	5.899	6.082
δ_J	0.021	0.022	0.023(8)	0.020	0.018	0.026	0.023	0.020	0.023
δ_K	0.259	0.219	0.146(126)	0.211	0.207	0.215	0.218	0.213	0.204

[a] Number of frequencies fitted.
[b] Standard deviation (kHz).

TABLE III. Calculated[a] and observed frequencies (cm^{-1}) for 1-fluoro-1-silacyclopentane *twisted* (C_1) form.

Vib. no.	Approximate description	*Ab initio*	Fixed scaled[b]	IR intensity	Raman activity	dp ratio	Observed IR gas	Observed Raman liquid/pol.[c]	Observed IR solid	P.E.D.[d]	Band Contour A	B	C
ν_1	α-CH_2 antisymmetric stretch	3179	2982	16.8	44.8	0.67	2966	2959	...	$65S_1, 23S_2$	2	18	80
ν_2	α-CH_2 antisymmetric stretch	3177	2981	6.6	105.9	0.59	2964	2955	2938	$66S_2, 22S_1$	49	8	42
ν_3	β-CH_2 antisymmetric stretch	3157	2962	30.2	49.4	0.75	2959	2947	...	$91S_3$	6	44	50
ν_4	β-CH_2 antisymmetric stretch	3151	2956	26.9	132.4	0.31	2954	2944	2923	$85S_4, 12S_8$	89	...	11
ν_5	α-CH_2 symmetric stretch	3109	2917	7.0	68.4	0.20	2911/2938	2911	2905	$52S_5, 39S_6$	48	39	13
ν_6	α-CH_2 symmetric stretch	3104	2912	10.0	77.9	0.22	2905	2902	2896	$50S_6, 37S_5$	16	9	75
ν_7	β-CH_2 symmetric stretch	3097	2905	25.3	45.0	0.35	2878	2870	2864	$87S_7$	...	27	73
ν_8	β-CH_2 symmetric stretch	3093	2902	21.2	139.8	0.10	2872	2864	2850	$78S_8, 11S_4, 10S_7$	98	1	1
ν_9	Si-H stretch	2310	2192	200.6	118.5	0.21	2175	2171	2169	$100S_9$	29	1	70
ν_{10}	β-CH_2 deformation	1566	1469	0.4	3.4	0.46	1466	1464/0.5	...	$94S_{10}$	100	...	...
ν_{11}	β-CH_2 deformation	1558	1462	6.5	18.5	0.75	1460	1455/dp	1450	$99S_{11}$	6	19	75
ν_{12}	α-CH_2 deformation	1513	1419	16.2	5.9	0.75	1412	1408/dp	1407	$82S_{12}, 16S_{13}$	...	77	23
ν_{13}	α-CH_2 deformation	1509	1416	4.7	20.9	0.74	1409	1405/dp	1401	$78S_{13}, 17S_{12}$	20	59	21
ν_{14}	β-CH_2 wag	1400	1329	1.2	3.8	0.75	1322	1321/dp	1341	$63S_{14}, 21S_{16}$	79	1	21
ν_{15}	β-CH_2 wag	1384	1313	1.9	0.6	0.75	1311	1311/dp	1306	$87S_{15}$	4	63	33
ν_{16}	β-CH_2 twist	1329	1261	8.7	7.4	0.72	1260	1259/0.6	1248	$45S_{16}, 33S_{20}$	96	1	3
ν_{17}	β-CH_2 twist	1326	1258	4.0	9.0	0.74	1255	1253/0.6	...	$48S_{17}, 19S_{21}, 18S_{19}$	67	31	2
ν_{18}	α-CH_2 twist	1267	1202	0.4	1.5	0.36	1199	1196/0.2	1196	$36S_{18}, 32S_{24}, 11S_{20}, 10S_{33}$	97	1	2
ν_{19}	α-CH_2 wag	1235	1171	2.1	3.5	0.75	1160	1156/dp	1152	$51S_{19}, 18S_{34}, 10S_{21}, 10S_{23}$	3	88	9
ν_{20}	α-CH_2 wag	1150	1091	60.6	5.3	0.74	1081	1081/0.4	1075	$37S_{20}, 21S_{16}, 12S_{32}, 10S_{14}$	97	...	3
ν_{21}	α-CH_2 twist	1088	1033	31.6	2.5	0.74	1036	1036/dp	1034/1026	$54S_{21}, 29S_{17}$	52	1	48
ν_{22}	Ring deformation	1082	1026	2.4	6.5	0.65	1021	1019/0.6	1017	$47S_{22}, 23S_{32}, 19S_{14}$	64	...	36
ν_{23}	Ring deformation	996	945	0.3	5.3	0.75	931	945/0.6	944	$31S_{23}, 22S_{19}, 14S_{34}, 12S_{29}$	...	...	100
ν_{24}	β-CH_2 rock	979	929	12.7	2.5	0.74	925	926/dp	924	$37S_{24}, 35S_{18}, 11S_{30}$	1	93	6
ν_{25}	Si–H perpendicular bend[e]	951	902	161.9	2.5	0.75	899	891/dp	893/885	$23S_{25}, 27S_{28}, 15S_{31}, 11S_{37}$	80	1	18
ν_{26}	Ring deformation	926	878	61.8	2.8	0.74	876	882/dp	873	$51S_{26}, 19S_{29}, 12S_{30}$	6	93	1
ν_{27}	Ring breathing	896	850	0.6	8.2	0.10	843	849/0.1	847	$43S_{27}, 23S_{32}, 16S_{22}$	3	17	80
ν_{28}	Si–F stretch	872	827	15.7	4.6	0.74	838	832/~dp	823	$58S_{28}, 27S_{25}$	23	35	43
ν_{29}	β-CH_2 rock	838	795	92.2	3.4	0.73	794	793/dp	789	$23S_{29}, 25S_{25}, 17S_{30}, 13S_{31}$	35	64	1
ν_{30}	Si–H parallel bend[e]	780	740	14.4	5.2	0.30	739	740/0.1	741	$19S_{30}, 22S_{33}, 17S_{31}, 10S_{27}$	10	52	38
ν_{31}	α-CH_2 rock	735	697	52.6	2.2	0.20	698	695/0.1	697	$16S_{31}, 18S_{33}, 18S_{23}$	20	66	13
ν_{32}	Ring deformation	697	661	3.7	12.2	0.21	676	678/0.1	680	$19S_{32}, 21S_{26}, 19S_{27}, 16S_{30}$	...	1	99
ν_{33}	α-CH_2 rock	638	605	5.8	7.9	0.33	609	614/0.1	614	$29S_{33}, 15S_{30}, 13S_{26}, 10S_{27}$	17	32	51
ν_{34}	Ring deformation	509	483	6.4	0.4	0.74	490	495/dp	492	$54S_{34}, 19S_{29}, 14S_{39}$	7	47	46
ν_{35}	Ring deformation	437	414	11.5	2.9	0.41	425	425/0.1	430	$71S_{35}$	44	8	47
ν_{36}	Ring twist	298	283	1.8	0.2	0.70		283/0.5		$63S_{36}, 18S_{38}$	6	84	10
ν_{37}	Si–F perpendicular bend[e]	278	263	4.8	0.5	0.69		271/0.4		$49S_{37}, 10S_{25}, 10S_{31}$	21	11	68
ν_{38}	Si–F parallel bend[e]	222	211	4.3	0.4	0.75		223/0.5		$62S_{38}, 25S_{36}$	...	99	1
ν_{39}	Ring puckering	83	79	1.5	0.1	0.71		...		$71S_{39}, 17S_{37}$	16	4	80

[a]MP2(full)/6–31G(d) *ab initio* calculations, frequencies from scaled force constants, infrared intensities (km/mol), Raman activities ($Å^4$/u), depolarization ratios (dp), and potential energy distributions (P.E.Ds).

[b]Scaling factors of 0.88 for CH_2 stretches and CH_2 deformations and 0.90 for all other modes except heavy atom bends.

[c]Experimentally obtained depolarization ratios.

[d]Symmetry coordinates with P.E.D. contribution less than 10% are omitted.

[e]Bend perpendicular and parallel to the ring, respectively.

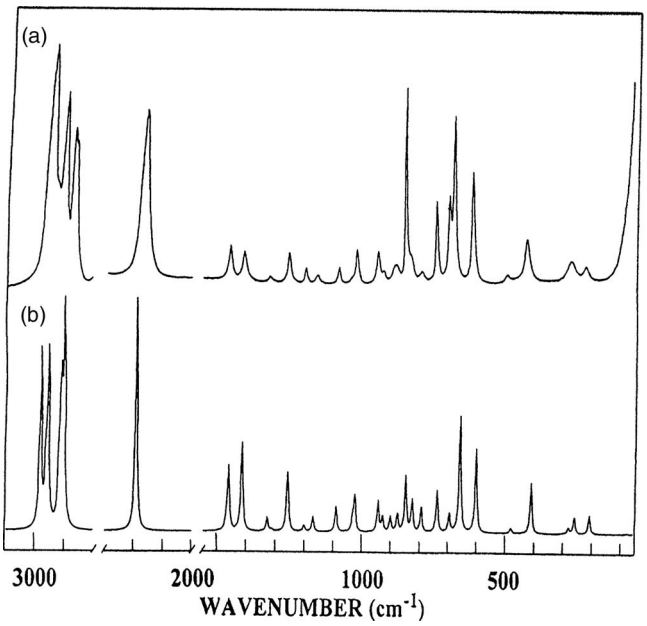

FIG. 2. Comparison of experimental and calculated Raman spectra of 1-fluoro-1-silacyclopentane: (a) observed spectrum of the liquid; (b) simulated spectrum of *twist* conformer (C_1).

in the Raman spectrum of the liquid along with their proposed assignments and depolarization ratios are listed in Table III.

The *ab initio* calculations were performed with the GAUSSIAN 03 program[13] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay.[18] Several basis sets as well as the corresponding ones with diffuse functions were employed with the Møller-Plesset perturbation method[19] to the second order (MP2(full)) as well as with the density functional theory by the B3LYP method. *Ab initio* calculations with a variety of high-level basis sets up to the aug-cc-pVTZ level were used to predict the energies of the four possible conformers, namely, *twist*, *envelope-axial*, *envelope-equatorial*, and *planar* forms. The *ab initio* calculations predict the *twist* form as the only stable conformer since the other three forms were found to be saddle points with at least one imaginary frequency from the MP2(full) predictions. The predicted conformational energy differences are listed in the supplemental material as Table S1.[39] The *envelope-axial* and *envelope-equatorial* forms have higher energies by ~1500 and 1700 cm^{-1}, respectively, than the *twist* form but they have much lower energies than the *planar* form which is at ~2400 cm^{-1}. Calculations from the B3LYP method follow the same trend but have lower energies than those from the corresponding MP2(full) method.

III. RESULTS

Since the microwave assignments included three isotopes for the Si atom and four different ^{13}C species, it should be possible to obtain structural parameters for the heavy atoms. Also, since the C–H distances can be predicted well from *ab initio* calculations and the Si–H distance from the frequency of the Si–H stretch, it should be possible to obtain the complete r_0 structure for this molecule. Therefore, we were interested in this aspect of the scientific study since we hoped to be able to compare the parameters obtained in this study with those previously obtained which were not extensively determined.

A. Structure

Rotational constants and dipole moment components from the MP2(frozen core)/6–311++G(2d,2p) *ab initio* calculations were used to predict the rotational spectrum. According to the predicted components of the dipole moment, which are $|\mu_a| = 1.87$ D, $|\mu_c| = 0.81$ D, and a relatively small value for $|\mu_b| = 0.07$ D, only *a*- and *c*-type transitions were predicted to have significant intensity. Based on the predicted spectrum, 33 of the observed transitions could be assigned easily to the most abundant isotopic species with rotational quantum number *J* up to 5 in the spectral region from 6000 to 18 000 MHz. It was also possible to assign 14 and 12 transitions for the ^{29}Si and ^{30}Si isotopes, respectively, and six to eight microwave lines for each of the remaining four singly substituted ^{13}C isotopomers in natural abundance (Table I). The three rotational and five quartic centrifugal distortion constants of an asymmetric rotor Hamiltonian (I^r orientation, *A* reduction[17]) were fit to the transition frequencies of the "normal" isotopologue with a standard deviation of 2.8 kHz. Since the number of observed transitions for the other isotopologues was too small to determine all eight constants for these species, the distortion constants used were predicted values from the B3LYP/6–311+G(d,p) calculations and kept constant during the fits to the asymmetric rotor Hamiltonian. The resulting rotational constants are listed in Table II.

The ground state rotational constants were used to determine the principal coordinates of the Si and C atoms by the Kraitchman method for single isotopically substituted species.[20] At least one principal coordinate for three of the ring atoms was very small, where, two of them even led to imaginary values, and some structural parameters of the heavy-atom ring structure of 1-fluoro-1-silacyclopentane derived from these coordinates have large deviations from the values predicted by the MP2(full)/6–311+G(d,p) *ab initio* calculations. These deviations from the predicted values raised serious questions regarding their reliability (Table IV).

We then used another approach to derive structural parameters particularly since there were a total of 21 rotational constants from the seven isotopomers of 1-fluoro-1-silacyclopentane that could be used to obtain "adjusted r_0" heavy atom parameters. We have found that good structural parameters can be determined by adjusting the structural parameters obtained from the MP2(full)/6–311+G(d,p) calculation to fit the rotational constants obtained from microwave experimental data by using a computer program "A&M" (*ab initio* and microwave) developed[21] in our laboratory. In order to reduce the number of independent variables, the structural parameters are separated into sets according to their types where bond distances in the same set keep their relative ratio and bond angles in the same set keep their difference in

TABLE IV. Structural parameters (Å and degree) and rotational constants (MHz) for 1-fluoro-1-silacyclopentane *twisted* (C_1) form.

Structural parameters	Internal coordinates	MP2(full)/ 6–311+G(d,p)	B3LYP/ 6–311+G(d,p)	r_s values[a]	Adjusted r_0
r (Si_1–C_2)	X_1	1.877	1.887	1.875 (1.868)	1.875(3)
r (Si_1–C_3)	X_2	1.874	1.884	1.841 (1.864)	1.872(3)
r (C_2–C_4)	Y_1	1.546	1.553	1.535 (1.542)	1.549(3)
r (C_3–C_5)	Y_2	1.545	1.551	1.570 (1.541)	1.547(3)
r (C_4–C_5)	Z	1.537	1.544	1.568 (1.529)	1.542(3)
r (Si_1–F_6)	r_1	1.633	1.641		1.598(3)
r (Si_1–H_7)	r_2	1.475	1.484		1.479(2)
r (C_2–H_8)	r_3	1.097	1.096		1.097(2)
r (C_3–H_9)	r_4	1.097	1.097		1.097(2)
r (C_2–H_{10})	r_5	1.093	1.092		1.093(2)
r (C_3–H_{11})	r_6	1.093	1.092		1.093(2)
r (C_5–H_{12})	r_7	1.097	1.096		1.097(2)
r (C_4–H_{13})	r_8	1.097	1.097		1.097(2)
r (C_5–H_{14})	r_9	1.094	1.094		1.094(2)
r (C_4–H_{15})	r_{10}	1.094	1.094		1.094(2)
$\angle C_3Si_1C_2$	θ	96.5	96.7	97.6 (96.7)	96.7(5)
$\angle Si_1C_2C_4$	ψ_1	103.3	103.6	104.1 (103.5)	103.6(5)
$\angle Si_1C_3C_5$	ψ_2	102.6	103.0	102.8 (102.7)	102.9(5)
$\angle C_2C_4C_5$	φ_1	108.3	109.1	107.6 (108.6)	108.4(5)
$\angle C_3C_5C_4$	φ_2	107.7	108.7	107.5 (108.2)	108.1(5)
$\angle F_6Si_1H_7$	α	105.7	105.3		105.2(5)
$\angle H_8C_2H_{10}$	γ_1	107.3	106.9		107.3(5)
$\angle H_9C_3H_{11}$	γ_2	107.4	107.1		107.4(5)
$\angle H_{13}C_4H_{15}$	ε_1	107.1	106.6		107.1(5)
$\angle H_{12}C_5H_{14}$	ε_2	107.2	106.7		107.2(5)
$\angle F_6Si_1C_2$	β_1	110.7	110.6		110.7(5)
$\angle F_6Si_1C_3$	β_2	111.1	111.4		111.6(5)
$\angle H_7Si_1C_3$	β_3	116.1	116.1		116.1(5)
$\angle H_7Si_1C_2$	β_4	116.6	116.8		116.5(5)
$\angle H_8C_2Si_1$	π_1	108.5	108.5		108.5(5)
$\angle H_9C_3Si_1$	π_5	109.8	109.4		109.8(5)
$\angle H_{10}C_2Si_1$	π_3	115.3	114.8		115.3(5)
$\angle H_{11}C_3Si_1$	π_7	114.4	114.1		114.4(5)
$\angle H_8C_2C_4$	π_2	109.8	110.5		109.7(5)
$\angle H_9C_3C_5$	π_6	109.5	110.2		109.4(5)
$\angle H_{10}C_2C_4$	π_4	112.6	112.5		112.4(5)
$\angle H_{11}C_3C_5$	π_8	113.1	113.0		112.9(5)
$\angle H_{12}C_5C_4$	σ_6	108.9	109.1		108.7(5)
$\angle H_{13}C_4C_5$	σ_2	108.5	108.9		108.5(5)
$\angle H_{14}C_5C_4$	σ_8	111.4	111.1		111.2(5)
$\angle H_{15}C_4C_5$	σ_4	111.5	111.2		111.5(5)
$\angle H_{12}C_5C_3$	σ_5	109.5	109.3		109.5(5)
$\angle H_{13}C_4C_2$	σ_1	109.5	109.3		109.6(5)
$\angle H_{14}C_5C_3$	σ_7	112.0	111.8		112.0(5)
$\angle H_{15}C_4C_2$	σ_3	111.8	111.2		111.8(5)
τ $Si_1C_2C_4C_5$	τ_1	−35.3	−33.1	−34.2 (−34.1)	−34.3(5)
τ $C_2C_4C_5C_3$	τ_2	51.4	48.3	49.4 (49.7)	49.9(5)
A		4672.7	4625.5		4700.4
B		2350.5	2320.7		2368.5
C		1900.5	1869.5		1903.6

[a]Values in parentheses were determined after corrections were applied by the vibration-rotation constants calculated from the cubic and scaled quadratic force fields from MP2(full)/6–31G(d) calculations.

degrees. This assumption is based on the fact that errors from *ab initio* calculations are systematic.

We[22] have also recently shown that *ab initio* MP2(full)/6–311+G(d,p) calculations predict the r_0 structural parameters for more than fifty carbon-hydrogen distances to better than 0.002 Å compared to the experimentally determined values from isolated C–H stretching frequencies[23] by comparison to previously determined values from earlier microwave studies. Therefore, all of the carbon-hydrogen distances can be taken from the MP2(full)/6–311+G(d,p)

TABLE V. Comparison of rotational constants (MHz) obtained from modified *ab initio* MP2(full)/6–311+G(d,p) predictions, experimental values from microwave spectra, and the adjusted r_0 structural parameters for 1-fluoro-1-silacyclopentane.

Isotopomer	Rotational constant	MP2(full)/ 6–311+G(d,p)	Expt.	Adjusted r_0	$\|\Delta\|$
c-$C_4H_8{}^{28}$SiHF	A	4672.7	4700.2	4700.4	0.2
	B	2350.5	2368.5	2368.5	0.0
	C	1900.5	1903.5	1903.6	0.1
c-$C_4H_8{}^{29}$SiHF	A	4662.6	4690.8	4690.8	0.1
	B	2341.5	2359.5	2359.5	0.0
	C	1896.2	1899.2	1899.2	0.0
c-$C_4H_8{}^{30}$SiHF	A	4652.9	4681.7	4681.6	0.1
	B	2332.9	2350.8	2350.7	0.1
	C	1892.0	1895.0	1895.0	0.0
$^{13}C_1$	A	4590.0	4616.9	4616.8	0.1
	B	2348.2	2366.3	2366.3	0.0
	C	1885.1	1888.3	1888.4	0.1
$^{13}C_2$	A	4588.4	4615.0	4615.1	0.1
	B	2347.5	2365.7	2365.6	0.1
	C	1885.9	1889.1	1889.0	0.1
$^{13}C_3$	A	4655.0	4682.0	4681.9	0.1
	B	2315.4	2333.0	2333.0	0.0
	C	1874.6	1877.6	1877.6	0.0
$^{13}C_4$	A	4636.0	4664.1	4664.0	0.1
	B	2321.5	2338.7	2338.8	0.1
	C	1879.0	1881.8	1881.8	0.0

predicted values for 1-fluoro-1-silacyclopentane. It has also been shown that Si–H distances can be obtained from the frequencies of the isolated Si–H stretching mode.[24] Therefore, we have obtained a value of 1.479 Å (Table IV) from the frequency of 2175 cm^{-1} which is 0.004 Å longer than the corresponding distance from the *ab initio* predicted parameters. This longer distance is approximately the same difference found for many Si–H distances in other organosilanes.[25,26] Thus, with the Si–H and C–H distances determined within 0.002 Å and the corresponding bond angles to an expected uncertainty of 0.5°, there were six distances, seven angles, and seven dihedral angles to be determined that involve heavy atoms. The resulting adjusted r_0 parameters that were determined for the *twist* form are listed in Table IV. It is interesting to note that the Si–F distances are much better predicted from RHF calculations than either the MP2(full) or B3LYP calculations used in this study.

The fit of the 21 rotational constants is given in Table V, with all of them agreeing to within 0.0 or 0.1 MHz except for one where the difference is 0.2 MHz. Therefore, it is believed that the C–C, C–Si, and Si–F distances have been determined to an uncertainty of ±0.003 Å with angle uncertainties of ±0.5°.

B. Vibrational assignment

Of primary interest was the determination of the conformation of the form or forms of 1-fluoro-1-silacyclopentane present in the fluid phases. Although *ab initio* calculations predict the *twist* form to have the lowest energy of the four possible conformers, there was a need to have experimental evidence to support the theoretical prediction. Therefore, the infrared spectrum of the gas was recorded first which was followed by recording the spectrum of the solid. A comparison of the two spectra (Figs. 1(a) and 1(b)) shows that all of the bands in the spectrum of the gas have corresponding bands in the spectrum of the solid. This concurrence indicates that there is probably only one conformer present in the gas phase unless the spectrum of the solid is that of an amorphous sample. We then recorded the Raman spectrum of the liquid (Fig. 2(a)) and found the observed bands had frequencies with very small shifts from those observed in the infrared spectrum of the gas. These results were taken to indicate, in this state, that there is little association and that no additional conformers were present in the liquid than those present in the gas. Thus, it was concluded that there was only one conformer present in the fluid states, which must be the *twisted* form based on the microwave data and the vibrational assignment was initiated.

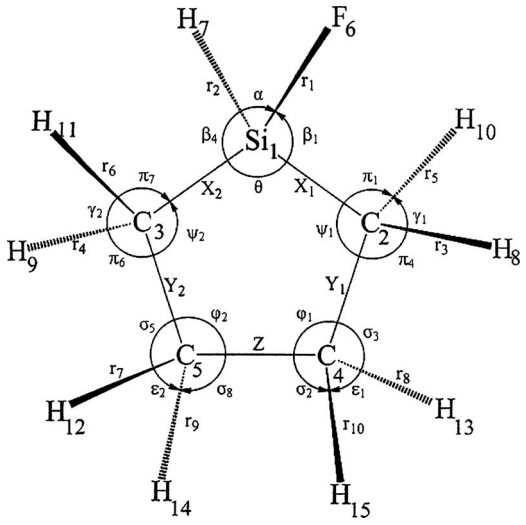

FIG. 3. *Planar* (C_s) conformer of 1-fluoro-1-silacyclopentane showing atom numbering and internal coordinates.

In order to obtain a complete description of the molecular motions involved in the fundamental modes of c-C_4H_8SiHF, a normal coordinate analysis had been carried out. The force field in Cartesian coordinates was obtained with the GAUSSIAN 03 program[13] at the MP2(full) level with the 6–31G(d) basis set. The internal coordinates used to calculate the G and B matrices are given in Table IV with the atomic numbering shown in Fig. 3. By using the B matrix,[27] the force field in Cartesian coordinates was converted to a force field in internal coordinates. Subsequently, scaling factors for the force constants of 0.88 for the CH_2 stretches and CH_2 deformations, and 0.90 for the other force constants except those for the heavy atom bends were applied, along with the geometric average of the scaling factors for the interaction force constants, to obtain the fixed scaled force field for computing the resultant wavenumbers. A set of symmetry coordinates was used (Table S2) (Ref. 39) to determine the corresponding potential energy distributions (P.E.Ds).

The vibrational spectra were predicted from the optimized structure and force field from MP2(full)/6–31G(d) calculations. In addition to the predicted frequencies from the scaled force constants, infrared intensities were obtained based on the dipole moment derivatives with respect to Cartesian coordinates also from the scaled force constants. The derivatives were transformed with respect to normal coordinates by $(\partial\mu_u/\partial Q_i) = \sum_j (\partial\mu_u/\partial X_j)L_{ij}$, where Q_i is the ith normal coordinate, X_j is the jth Cartesian displacement coordinate, and L_{ij} is the transformation matrix between the Cartesian displacement coordinates and the normal coordinates. The infrared intensities were then calculated by $(N\pi)/(3c^2)$ $[(\partial\mu_x/\partial Q_i)^2 + (\partial\mu_y/\partial Q_i)^2 + (\partial\mu_z/\partial Q_i)^2]$ and the simulated spectra were plotted by using a Lorentzian function. A comparison of experimental and simulated infrared spectra of c-C_4H_8SiHF is shown in Fig. 1.

Additional support for the vibrational assignments was obtained from the simulated Raman spectra. The evaluation of Raman activity by using the analytical gradient methods has been developed[28–31] and the activity S_j can be expressed as: $S_j = g_j(45\alpha_j^2 + 7\beta_j^2)$, where g_j is the degeneracy of the vibrational mode j, α_j is the derivative of the isotropic polarizability, and β_j is the anisotropic polarizability. To obtain the Raman scattering cross sections, the polarizabilities are incorporated into S_j by multiplying S_j with $(1 - \rho_j)/(1 + \rho_j)$ where ρ_j is the depolarization ratio of the jth normal mode. The Raman scattering cross sections and calculated wavenumbers obtained from the scaled force constants were used together with a Lorentzian function to obtain the simulated Raman spectra. Comparison of experimental spectra of the liquid and the predicted spectra for the *twist* conformer are shown in Fig. 2. The experimentally determined depolarization ratios are listed in Table III for comparison to those obtained from the MP2(full)/6–31G(d) calculation. A relatively large number of the predicted polarization values are depolarized, whereas many of the experimental polarization values are significantly smaller than those predicted. Nevertheless, they contributed in making the vibrational assignment.

By utilizing the frequencies from the scaled force constants, the predicted infrared band contours and intensities along with the predicted Raman activities and depolarization values, the vibrational assignments were made. A number of the fundamental vibrations could be initially assigned from well-known "group frequencies" particularly in the "fingerprint" region. The most uncertain assignments for the carbon-hydrogen motions were for the CH_2 stretches where eight normal modes were grouped together with significant Fermi resonance also expected. More confident assignments can only be made, in this spectral region, by utilizing deuterium substitution first for the α-CH_2 groups and then the β-CH_2 groups. However, most of the carbon-hydrogen bending modes could be assigned by "group frequencies" except for the lower frequency ones which are extensively mixed with the heavy atom motions. The vibrations of most interest are the nine heavy atom ring motions. These modes have been extensively studied for substituted cyclopentanes but there is very limited vibrational information for 1-silacyclopentanes and 1-germacyclopentanes.

From the earlier studies[7,8] on the two cyclopentane molecules which had silicon in the ring, there were four ring modes in the region of 1050–840 cm^{-1}. These four modes are usually mixed with the CH_2 and the Si–H bends. Therefore, their descriptions are usually supported by modest P.E.D. predictions and their assignment is not questionable. In the current case, the three deformations can be assigned based upon the band contours as well as their relative intensities in the Raman spectra. The lower frequency deformation is usually not as extensively mixed and has a strong intensity in the infrared spectra whereas the ring breathing mode is mainly assigned from the Raman spectra. Thus, these four fundamentals have been assigned in the expected frequency ranges. The next three deformations are usually below 700 cm^{-1} and span the region with one of them in the mid 600 cm^{-1} range and the other two in the 400 cm^{-1} region. Again, their assignments could be made in these regions but it is clear from the P.E.D. that the one at 676 cm^{-1} region is so extensively mixed with two other ring modes resulting in near equal contributions, i.e., $19S_{32}$, $21S_{26}$, and $19S_{27}$. Therefore, the description of the ring mode at 676 cm^{-1} is more for convenience than the description of the primary atomic motions. The two lower frequency ring deformations in the 400 cm^{-1} region are assigned based on the band contours and predicted frequencies and there are relatively small contributions from other modes, particularly for the lower frequency deformation.

The final two ring modes are the ring twist and the ring puckering vibrations with the twist assigned at 283 cm^{-1} from the Raman spectra but the ring puckering was not observed. However, it was predicted at 79 cm^{-1} and it is expected that this frequency is a reasonable estimate of this vibration.

IV. DISCUSSION

The vibrational assignments for the fundamentals of the *twist* form of c-C_4H_8SiHF were made possible mainly from the predictions of the frequencies, followed by the band contours and finally the infrared intensities and Raman activities. This is illustrated well where the frequencies from the predicted force constants for the fundamental vibrations involving two scaling factors compare quite favorably with the observed values with an average error of 8 cm^{-1} which represents a percent error of 0.5% for the *twist* conformer. This error also includes vibrations from the carbon-hydrogen stretching motions with some of the greatest contributions to the error coming from the β-CH_2 symmetric stretches and Si–H stretch. Nevertheless, the advantage of the *ab initio* MP2(full)/6–31G(d) calculation is highlighted by the fact that the observed frequencies are relatively close or usually lower than the predicted values.

The rigid C_1 symmetry ring framework of the *twist* conformer has an energy difference of 2316 cm^{-1} to the C_s symmetry *planar* form from the MP2(full) calculations utilizing the largest basis set, aug-cc-pVTZ (487 basis functions), with a much smaller value of 1761 cm^{-1} from the corresponding B3LYP method. This result indicates that the *planar* form would not be the route chosen by the molecule going from one *twist* form to another. Instead, the molecule may go through a series of *twisted* forms where one atom moves out

perpendicular to a hypothetical plane containing the rest of the atoms, possibly encountering the *envelope* forms also in the process.

The predicted infrared intensities and band contours contributed significantly to the vibrational assignment but some of the Raman activities were poorly predicted. Of particular note was the ring breathing mode (ν_{27}) which is expected to give rise to a relatively strong Raman line which it does but the predicted Raman band is relatively weak. We have found similar problems in several other ring molecules. There are three other modes, i.e., ν_{11}, ν_{13}, and ν_{31}, where, the predicted Raman intensities are relatively poor. Thus, the Raman activities are not nearly as useful for making vibrational assignments as are the infrared intensities.

Applying the idea behind the derivation of "semi-experimental" r_e structure,[32–34] the ground state rotational constants were corrected by the vibration-rotation constants calculated from the cubic and scaled quadratic force fields from MP2(full)/6–31G(d) *ab initio* calculations to obtain semi-experimental equilibrium rotational constants.[32] These estimated constants were used with the Kraitchman equations to derive estimated equilibrium principal coordinates (none of them imaginary), and the structural parameters derived from them were, for the most part, in better agreement with the MP2(full)/6–311+G(d,p) predictions and with the adjusted r_0 structures (see next paragraph) but still not satisfactory.

Apparently, the semi-experimental equilibrium rotational constants (from MP2(full)/6–31G(d) force fields) are not sufficiently corrected to give reliable structural data. Although satisfactory results have been obtained for semi-experimental structures of many molecules by using MP2(full)/6–31G(d) force fields,[32,35,36] this method did not work as well for 1-fluoro-1-silacyclopentane. Two possible reasons for this come to mind: (i) the three different atoms with at least one very small principal coordinate combined with just a minimal set of experimental rotational constants may have pushed this method to the limit; (ii) the MP2(full)/6–31G(d) force fields may not be sufficiently precise when both Si and F are present. An indication that part of the blame lies in the force field is the quartic centrifugal distortion constants derived from it which had deviations considerably larger than 10% or so from the observed constants than usual.[32,37,38] On the other hand, the 6–311+G(d,p) basis set utilizing both the MP2(full) and B3LYP methods predicted distortion constants in much closer agreement with the experimentally determined values (Table II).

Based on the fit of the rotational constants obtained for the r_0 structural parameters, it is indicative that the relative distances between the carbon atoms in this 5-membered ring have been well determined and provide significantly improved parameters than the r_s values. The estimated uncertainties are reasonable and the r_0 values obtained from this study are probably as good as could be obtained from electron diffraction investigation or from the use of significantly larger number of substituted atoms. In general, when the atoms are near to an axis, the r_s values are relatively difficult to obtain to provide meaningful distances. Since there are very few 5-membered rings containing a silicon atom where the structural parameters have been obtained, it is difficult to provide a comparison of the parameters for these molecules. The fluorine atom is expected to cause a significant reduction in the C–Si distance compared to the distance for the corresponding molecule where chlorine is the substituted halogen. An estimated distance has been reported[7] which is significantly longer. It would be of interest to investigate the microwave spectra of c-C_4H_8SiHCl to ascertain the structural parameters of another halogen silacyclopentane, which would help in obtaining structural parameters that could be transferred for larger molecules that might contain the 5-membered ring with silicon.

All three of the 1-halo-silacyclopentanes have the *twisted* form as the stable conformer.[7,8] A comparison of the energies of the three saddle points, i.e., *envelope-axial*, *envelope-equatorial*, and *planar* forms, have energies for the *planar* forms nearly the same. For the *axial* forms, the fluoro molecule has an energy difference about 200 cm^{-1} higher than the other two molecules, whereas all three *equatorial* forms have nearly the same values.

Comparing the corresponding carbon compounds, it is interesting to note that the fluoride molecule has the *twisted* form as the stable conformer, which is the same in the silicon-containing molecules. However, the other two carbon compounds have the *envelope-axial* form as the lower energy conformer than the *envelope-equatorial* form with enthalpy differences of 145 ± 15 cm^{-1} (1.73 ± 0.18 kJ mol^{-1}) and 233 ± 23 cm^{-1} (2.79 ± 0.27 kJ mol^{-1}) for the chloride and bromide, respectively. The *twisted* form for both these molecules is a saddle point as is the *planar* form with relatively similar small energy differences of ~800 cm^{-1} with respect to the *axial* form.

It would be of interest to investigate the conformational stabilities of 1-chloro-germacyclopentane and the corresponding bromo compound to find if these molecules have structures similar to those of the carbon molecules or those of the silicon compounds particularly since some germanium compounds have more similarities to the carbon molecules than do the silanes.

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[39]See supplementary material at http://dx.doi.org/10.1063/1.3673889 for Table S1: calculated electronic energies (Hartree) and energy differences (cm^{-1}) for the *twisted*, *envelope*, and *planar* conformers of 1-fluoro-1-silacyclopentane; and Table S2: the symmetry coordinates of 1-fluoro-1-silacyclopentane.